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THERMAL BEHAVIOUR OF POLY(METHYL METHACRYLATE) STEREOCOMPLEX BY DTA

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ABSTRACT

In this paper, the thermal properties of poly(methyl methacrylate) stereocomplex obtained in co-solvent binary mixtures have been examined. Two melting temperatures in the stereocomplex were found, which correspond to two different steps in the formation of a stereocomplex precipitate. Also, the influence of co-solvent power in the melting behaviour of the solid stereocomplex was determined.

INTRODUCTION

On mixing solutions of isotactic and syndiotactic poly(methyl methacrylate) (PMMA) a stereocomplex is formed by intermolecular association. This phenomenon occurs in most solvents, but to different extents [1–7].

Solvents can be classified into three groups according to their behaviour: the strongly complexing type, A, the weakly complexing type, B, and the non-complexing type, C [1].

It has been found that the stereocomplex has a crystalline structure as shown by X-ray analysis [2].

Bosscher et al. [8] found that ester groups from the isotactic chain and α-methyl groups from the syndiotactic chain are responsible for the stereocomplex formation.

Most investigators [4,9–13] report an optimum ratio of iso and syndiotactic PMMA in the stereocomplex of 1/2, but ratios of 1/1 and 1/1.5 have also been reported [14–18].

The influence of solvent on the stereocomplex formation has also been studied by viscometry [1,4], ultracentrifugation [10] and NMR [14,15], and in very few cases by DTA. The heat of formation of the stereocomplex has been studied in several solvents by Biros et al. [11]. de Boer and Challa [19] have studied the melting behaviour of the stereocomplex obtained in acetone and DMF.

In this paper, the influence of solvent quality on the stereocomplex melting behaviour is examined. The three binary co-solvent mixtures chosen were: acetonitrile/ carbon tetrachloride, acetonitrile/butyl chloride and butyl chloride/carbon tetrachloride. All solvents employed in these binary mixtures are of type A, i.e. strongly complexing.

EXPERIMENTAL

Isotactic PMMA was prepared by polymerization of MMA (Fluka purum) in toluene at low temperature with phenyl magnesium bromide as initiator [20].

Syndiotactic PMMA was obtained by anionic polymerization in THF solution initiated with diphenyl sodium [21].

The average molecular weight values, $\overline{M}_w$, of both samples were determinated by light scattering. The values obtained for it- and st-PMMA were 6.6×10^5 and 1.7×10^5, respectively.

The stereocomplex was prepared by mixing, in the ratio 1/2, 0.2 g dl^{-1} solutions of it- and st-PMMA in the binary mixture. The mixed solutions were kept in a thermostatically controlled bath at 30.0°C for one day. The precipitate was separated from the solution in a centrifuge with an acceleration of 22,000 g and then dried in vacuum at room temperature.

The calorimetric measurements were carried out in a differential thermal analyzer, Mettler TA 2000 system, with a heating rate of 5°C min^{-1}. The data were calibrated in absolute units by comparing with the specific heat of a sample of indium.

The thermal behaviour of the stereocomplex was studied in the temperature interval 30–230°C. The absolute temperature was calculated by the equation

$$T_{s_1} = T_{p_1} - \tau \frac{dT_p}{dt} + \frac{\Delta U_1}{s}$$

where T_{s_1} and T_{p_1} are the sample and program temperatures at point T_1 (°C), respectively, τ is an intrinsic constant of DTA, with a value of 0.5, dT_p/dt is the heating rate, ΔU_1 is the signal at point T_1(μV), and S is the sensitivity of the thermocouple.

All measurements were made using aluminium crucibles and stereocomplex samples ranged between 3 and 8 mg. Samples were weighed on a Mettler balance model H 51 AR with a precision of 5×10^{-5} g.

RESULTS AND DISCUSSION

The thermograms of the stereocomplex cannot be performed at all solvent binary mixture compositions due to the absence of a precipitate at certain compositions [$0.2 < u_2 < 0.9$ for the acetonitrile (1)/carbon tetrachloride (2) mixture and $0.4 < u_2 < 0.7$ for the acetonitrile (1)/butyl chloride (2) mixture; a precipitate was obtained in the whole range of compositions for the butyl chloride (1)/carbon tetrachloride (2) mixture].

This can be explained by taking into account the loss of the "strongly complexing" character of the co-solvent binary mixture. This behaviour does not allow the precipitation of the stereocomplex by ultracentrifugation, due to the absence of clusters of high molecular weight.

Two endothermic peaks were found in the thermograms in the tempera-

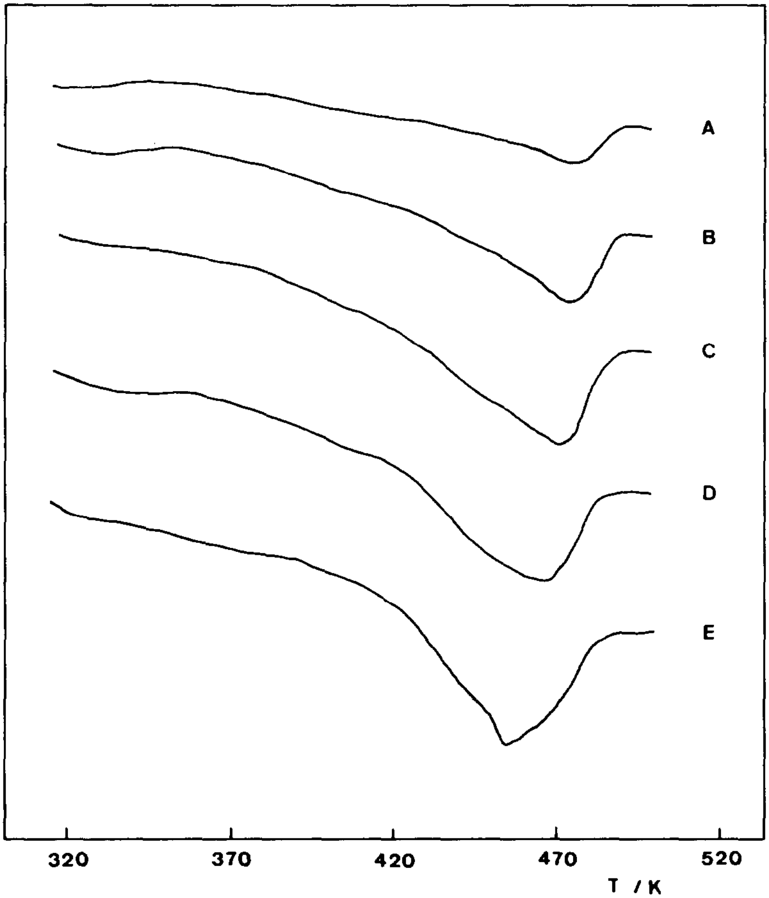

Fig. 1. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture acetonitrile (1)/carbon tetrachloride (2) at u_2 values of: A, 0.15; B, 0.13; C, 0.10; D, 0.05; E, 0.00.

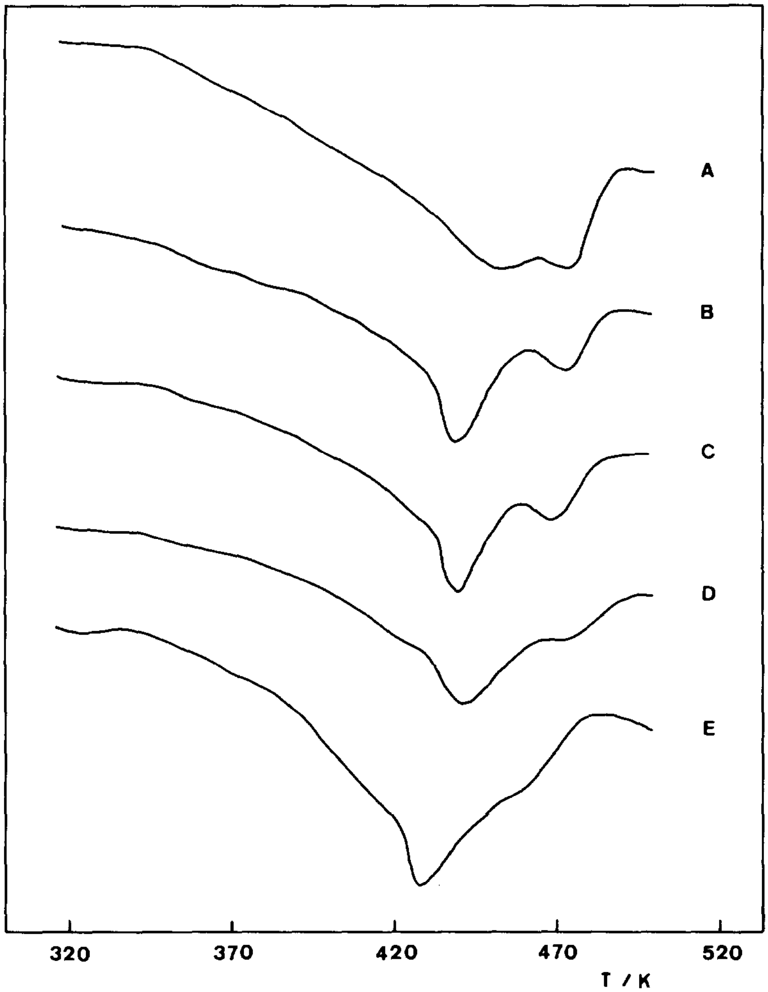

Fig. 2. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture acetonitrile (1)/carbon tetrachloride (2) at u_2 values of: A, 0.95; B, 0.96; C, 0.97; D, 0.99; E, 1.00.

ture range 155–207°C. These peaks are characteristic of two different melting temperatures (T_{m1} and T_{m2}). Challa and co-workers [13] have shown that both peaks are due to two different crystallizations of the stereocomplex, and not to the melting of crystalline it- or st-PMMA.

Figures 1–4 show the solvent influence on both melting temperatures and the ratio of the peak areas, which are related to the variation of the heat of fusion, ΔH_f, and therefore with crystallinity. So, the peak areas ratio indicates the contribution of the two processes to the phenomenon.

On going away from both pure liquids the first endothermic peak decreases with respect to the second one. This effect is accompanied by a decrease of stereocomplex precipitate.

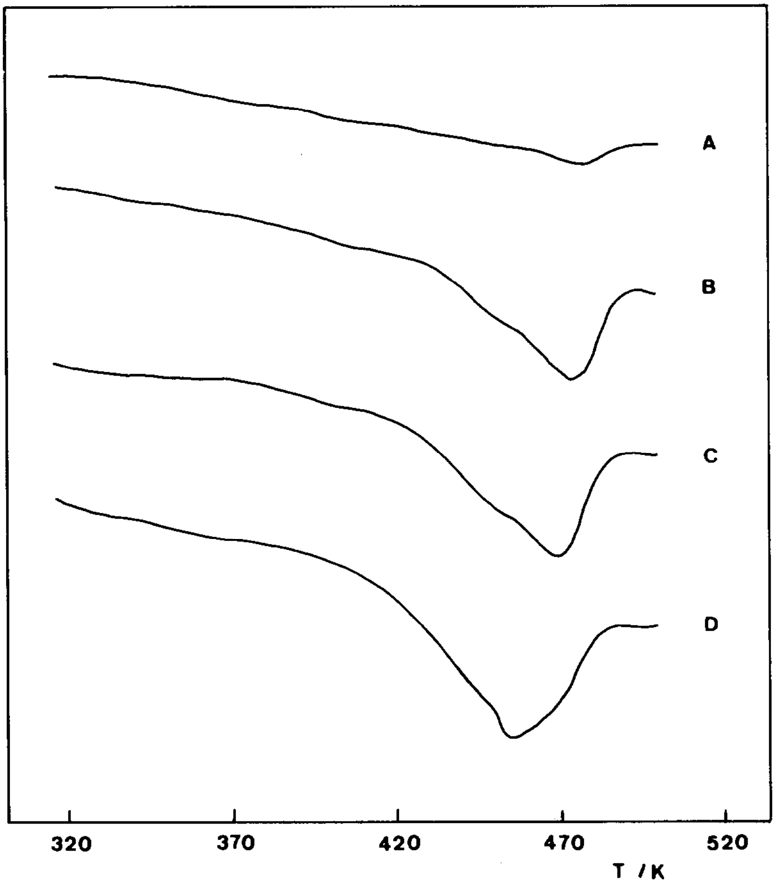

Fig. 3. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture acetonitrile (1)/ butyl chloride (2) at u_2 values of: A, 0.30; B, 0.20; C, 0.10; D, 0.00.

We propose that the second peak (T_{m_2}) corresponds to the stereocomplex formation and the first one (T_{m1}) to aggregates of stereocomplex ("clusters"). As stereocomplex interactions (intermolecular forces of first class) are stronger than cluster interactions (intermolecular forces of second class), it is reasonable that the melting temperature of the former are greater than the melting temperature of the latter. On the other hand, the second peak is almost independent of the co-solvent power of the binary mixture (as can be seen in Figs. 1–6 if the curves are normalized). This means that, at least, at binary mixture compositions in which a stereocomplex precipitate is obtained, this crystallization is not strongly affected by solvent power.

In the butyl chloride (1)/carbon tetrachloride (2) system the composition influence on T_{m_1}, T_{m_2} and their areas is negligible (Figs. 5 and 6) due to the small variation of the solvating power for this mixture in the whole range of compositions [22].

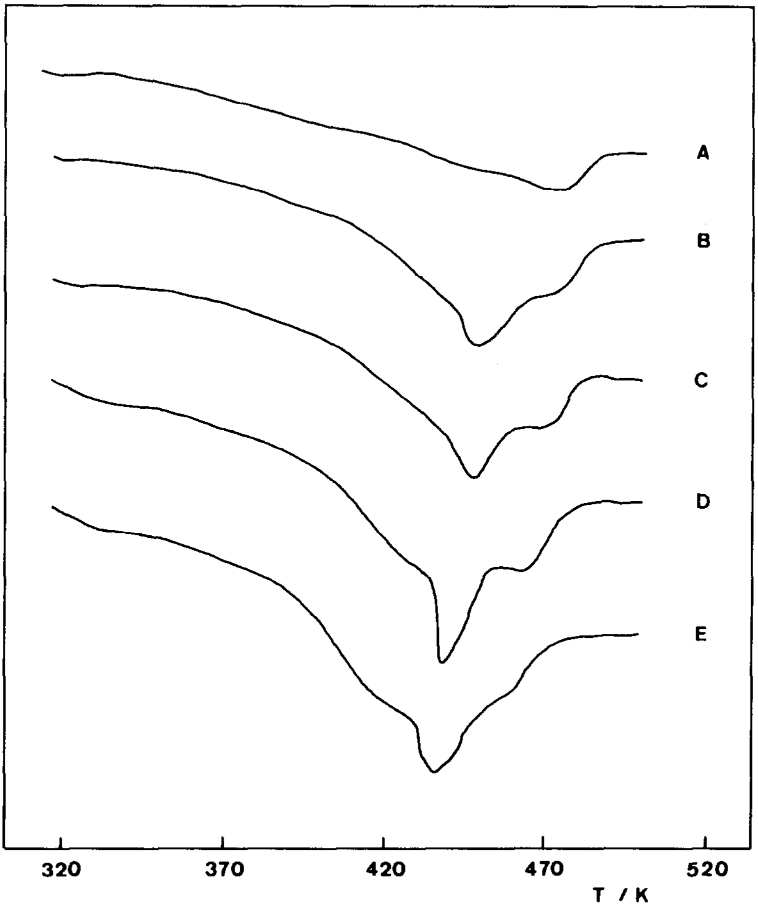

Fig. 4. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture acetonitrile (1)/butyl chloride (2) at u_2 values of: A, 0.80; B, 0.85; C, 0.90; D, 0.95; E, 1.00.

The complexing character variation in these binary mixtures has been shown by Katime and Ochoa [23] on studying the it-PMMA association by V.P.O.

This behaviour can be explained by taking into account the excess Gibbs

TABLE 1

Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture acetonitrile (1)/carbon tetrachloride (2)

	u_2							
	0	0.05	0.10	0.13	0.15	0.95	0.97	1
T_{m_1}(°C)	183	177	175	175		179	166	155
T_{m_2}(°C)	195	195	199	203	205	201	198	187

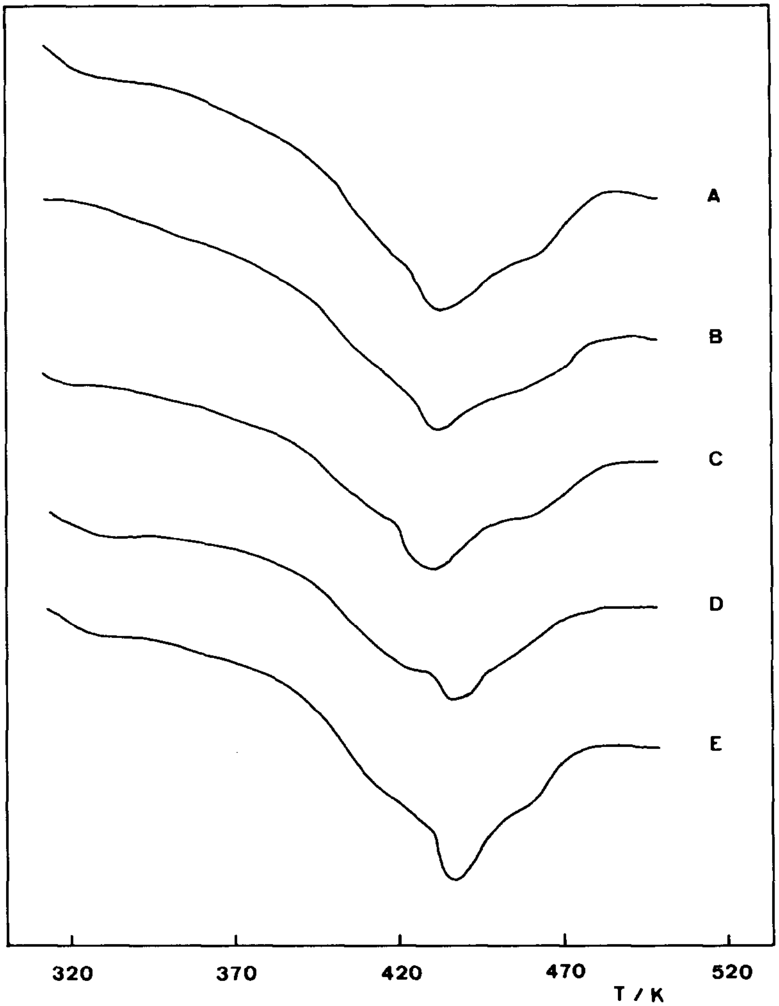

Fig. 5. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture butyl chloride (1)/carbon tetrachloride (2) at u_2 values of: A, 0.50; B, 0.40; C, 0.30; D, 0.10; E, 0.00.

TABLE 2

Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture acetonitrile (1)/butyl chloride (2)

	u_2									
	0	0.10	0.20	0.30	0.70	0.80	0.85	0.90	0.95	1
T_{m1}(°C)	183	176	176	173		173	175	174	164	162
T_{m_2}(°C)	195	196	201	204	207	201	201	197	191	187

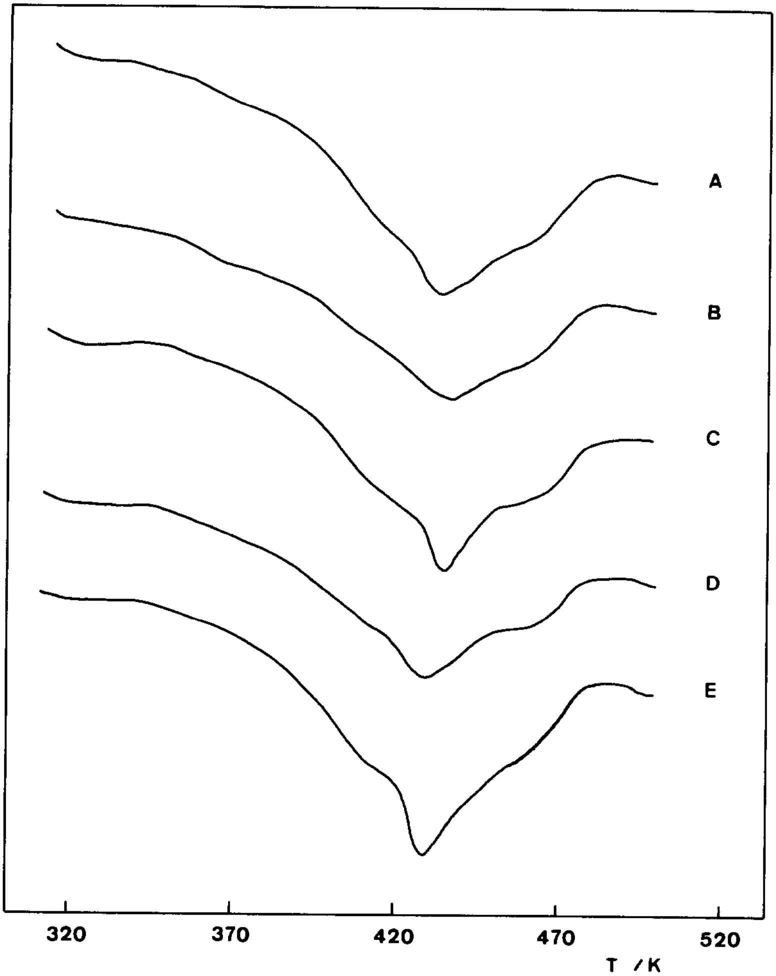

Fig. 6. Thermograms of different samples of stereocomplex obtained at different compositions of the binary mixture butyl chloride (1)/carbon tetrachloride (2) at u_2 values of: A, 0.50;B, 0.60; C, 0.70; D, 0.90; E, 1.00.

TABLE 3

Melting temperatures for different stereocomplex samples obtained at several compositions of the binary mixture butyl chloride (1)/carbon tetrachloride (2)

	u_2								
	0	0.10	0.30	0.40	0.50	0.60	0.70	0.90	1
T_{m_1}(°C)	162	160	159	159	159	162	161	157	155
T_{m_2}(°C)	187	187	189	189	191	191	192	191	187

free energy, G^E. In fact, we have found that G^E (butyl chloride/carbon tetrachloride) < G^E (acetonitrile/butyl chloride) < G^E(acetonitrile/carbon tetrachloride). This implies that solvent–solvent interactions increase as G^E decreases, and therefore polymer–solvent interactions decrease. This balance of interactions between the four components is the controlling force of the process.

The melting temperatures, T_{m_1} and T_{m_2}, are also influenced by the solvent power of the binary mixtures. In the Tables 1–3, it can be seen that T_{m_1} range between the T_{m_1} values obtained in pure solvents. On the contrary, T_{m_2} increases as the co-solvent power increases. This can be explained by taking into account that as the macromolecular coil increases, the ester groups of it-PMMA and the α-methyl groups of st-PMMA can interact more easily and to a greater extent. This implies that the complex formed is more stable, which is in accord with the experimental results shown in Figs. 1–6.

On the other hand, as the co-solvent power increases, the cluster formation decreases. The effect of this is that the quantity of stereocomplex obtained decreases, as stereocomplex–solvent interactions increase.

This behaviour of the melting temperatures was also found by de Boer and Challa [19] on studying stereocomplex formation as a function of temperature and it can be explained in the same way.

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